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ADVANCES IN CHEMICAL CONVERSIONS FOR MITIGATING CARBON DIOXIDE

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Iron Catalyzed CO_2 Hydrogenation to Liquid Hydrocarbons

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Many of the catalysts which are useful in Fischer-Tropsch synthesis are also capable of catalyzing the hydrogenation of CO_2 to hydrocarbons. Our structure-function studies have shown that it is possible to control the selectivity of CO_2 hydrogenation by specific iron-based catalysts to generate yields of C_5+ hydrocarbons that are comparable to those produced with conventional CO based feedstocks.

1. INTRODUCTION

Catalyst structure-function studies have shown that alpha-olefins are the primary products of CO_2 hydrogenation, with normal paraffins being formed by secondary hydrogenation. Catalysts that contain mainly iron oxide, or iron carbide with substantial concentrations of matrix carbon, favor secondary reactions and limited chain growth. The relative concentrations of these phases depend on the ease of reduction of the starting catalyst precursor, which can be changed to some degree by substitution of various cations into the initial formulation. In cases where excess matrix carbon is introduced into the reduced/carbided catalyst system, we are able to demonstrate the importance of diffusion constraints on overall process selectivity. We have developed proprietary iron catalysts that are essentially free of metal oxide and/or matrix carbon phases, with unprecedented selectivity toward C_5+ olefinic products.

2. BACKGROUND ON CO AND CO_2 HYDROGENATION

Studies on CO_2 hydrogenation can be traced back to the early 1900's [1] with emphasis on cobalt, nickel and iron-based catalysts. While this work clearly demonstrated the overall reactivity of CO_2 under a wide range of reaction conditions, the primary product(s) consisted of methane, CO and other light hydrocarbons. Emmett and others have evaluated the large body of experimental work that was performed through the early 1960's and concluded that CO_2 hydrogenation to higher molecular weight hydrocarbons remained a significant challenge.

Selectivity control continues to be a critical issue in Fischer-Tropsch chemistry, a catalytic process that dates back more than seventy years [1]. Operating conditions can be adjusted to control selectivities but overall effects are limited [2-4]. During Fischer-Tropsch synthesis with conventional bulk iron catalysts, various phases, including metal, metal carbides and metal oxides are present at steady-state catalytic conditions [5-7].

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Previous studies indicate that alkali increases the heat of CO chemisorption while decreasing the heat of H_2 chemisorption [8,9]. As a result of alkali promotion on iron catalysts, the average chain length and the olefin content of the products increase, whereas the activity and methane selectivity decrease [10,11].

Recent studies indicate that α-olefins, the major primary products formed during Fischer-Tropsch synthesis, participate in secondary reactions [12]. Chains can terminate either by β-hydrogen abstraction to form an α-olefin or by H-addition to form a paraffin [13,14]. Olefins can undergo secondary reactions by subsequent readsorption leading to isomerization or hydrogenation. We observe selectivity relationships that are consistent with Egiebor's proposal that significant secondary hydrogenation reactions can occur on iron catalysts [12].

3. EXPERIMENTAL ON CO AND CO_2 HYDROGENATION

The details of the preparation of the iron oxide catalyst precursors are described elsewhere [15-17]. For those carbides made by exsitu carburization, the oxide was loaded into a 1" diameter quartz tube and heated in a 1/1 H_2/CO mixture at a space velocity of 10,000 v/v/hr at 350°C for 24 hours. Iron carbide catalysts were also prepared by laser pyrolysis of iron carbonyl and ethylene using a 150 watt continuous wave CO_2 laser to provide both a rapid high temperature reaction (~.1 sec with T~1000°C) and quench [18].

The procedures used to produce the wet chemical and laser generated iron carbides of this paper have been disclosed in detail [22]. Catalyst tests were performed in a 300 cc Parr stirred tank reactor with octacosane as the slurry medium. Wide-angle powder x-ray diffraction identified catalyst phases present. Thermogravimetric reductions were recorded on a Mettler TA-2000°C using 100-200 mg of sample and a heating rate of 8 deg/min. Gravimetric titrations were performed using a specially designed heated entry port enabled injection of the pyridine titrant [19]. Mossbauer spectra were collected with an Austin Sciences instrument with a radiation source consisting of Co^{57} diffused into Rh (New England Nuclear).

4. RESULTS AND DISCUSSION

Unpromoted iron oxide catalysts (surface area 30-50m^2/gm) and iron oxide converted ex-situ to iron carbide were compared under standard reaction conditions. Figure 1 illustrates the sequential conversion of an iron surface in 1:1 H_2:CO at 1 atm under programmed heating conditions. In region 1 CO adsorbs onto the metal surface. At about 300°C, Fe begins to convert to (Haag) carbide and at slightly higher temperature amorphous carbon begins to grow. Gravimetric acidity titrations with 3,5 dimethylpyridene at 250°C showed an acid site concentration of 99 μ-moles/gm catalyst for the oxide and only 27 for the carbided catalyst. These numbers compare with ~250 μ-moles/gm for a solid acid like γ-Al_2O_3.

Figure 2 summarizes the different product selectivities measured at CO conversions of ~50%. In the carbided system we find ethylene present as well as a higher olefinic content in C_4, apparently as a result of inhibited secondary hydrogenation. Consequently, a carbided iron surface produces a more olefinic, heavier product, consistent with the observations of Egiebor and Cooper who suggest that acid sites on a precipitated $FeOx$/SiO_2 catalyst lead to secondary reactions of α-olefins [12].

Alkali titrates acid sites on the iron surface and also increases the strength of the CO-surface interaction. Figure 3 compares the effect of potassium promotion on the iron carbide catalyst where we had substantial amounts of matrix carbon. A cementite Fe_3C phase was synthesized by laser pyrolysis with a carbon content corresponding closely to the Fe_3C stoichiometry, i.e., without any excess matrix carbon. Some of it was heated in H_2/CO mixtures (1/1) at 350°C in order to introduce 40-50% by weight matrix carbon. Figure 4 shows that the excess carbon reduced olefin selectivity while favoring CH_4 and lighter products. The pure carbide, as prepared, does not respond to alkali treatment, Figure 5, suggesting that potassium is only needed when removal of the olefins is not fast enough to prevent secondary hydrogenation. The oxide catalyst reduces at lower temperature with substitution of Co into Fe_3O_4. Figure 6 shows the onset of reduction is initiated 20°C lower with the cobalt substitution. This may explain the enhanced olefin selectivity attributed to iron-cobalt catalysts in the literature [20,21].

Mossbauer spectroscopy on spent catalysts suggests that oxide/carbide phase formation in iron catalysts is also sensitive to reactor configuration (extent of backmixing). In integral fixed bed reactors, we find that iron has partitioned into carbide in the front of the bed but shows increasing amounts of oxide near the exit, whereas the same catalyst in the stirred tank reactor remains all iron carbide, Figure 7.

Comparative tests were conducted on CO_2 hydrogenation over a conventional coprecipitated Fe/Cu/K/Si catalyst versus a wet chemical derived sample of Fe_5C_2, see Figure 8. At 7/1 H_2/CO_2 feed ratio, the carbide exhibits significantly higher selectivity to C_2+ products and higher olefin yields than the conventional catalyst.

The higher molecular weight fractions produced from the 7/1 H_2/CO_2 feed consisted of a mixture of alpha- and beta-olefins, n-paraffins and n-alcohols together with large fraction of methyl-branched and internal olefin isomers, see Figure 9, while a 2/1 mixture of H_2/CO operated at >80% CO conversion (i.e., effective H_2/CO ratios >10/1) over this catalyst would produce nearly 65% alpha-olefin, 15% n-paraffin, 1-3% n-alcohol and 15% methyl-branched and internal olefin isomers.

Laser generated carbides that contain virtually no matrix carbon overlayer have been tested and show much higher selectivity to desired products than wet chemical analogs. The Zn and Mn containing systems required potassium promoters for optimum selectivity, see Figure 10.

A series of 13-CO_2 labeling studies were conducted to determine the extent of CO_2 conversion to hydrocarbons in the presence of varying quantities of CO, see Figure 11. These studies showed that no CO_2 was converted in mixtures where >5% carbon atom CO was present, and that CO_2 conversion to hydrocarbons did not occur until virtually all of the CO was consumed. Preliminary kinetic studies showed that product formation rates in the presence of low levels of unlabeled CO were consistent with a mechanism involving dissociative CO_2 chemisorption followed by "CO" and surface "C" formation with hydrogenation to hydrocarbons, Figure 12.

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ACKNOWLEDGMENTS

Figure 1
THERMAL CONVERSION OF IRON TO IRON CARBIDE

Fe in H2/CO at 1 atm

Wt

5%

T (°C)

100 200 300 400 500
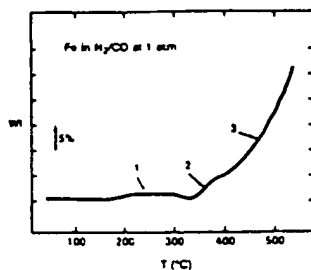
1—Low Temp. CO Adsorption
2—Oxide Converts to Carbide
3—Surface Carbon Grows

Figure 2. OXIDE SURFACE SHOWS MORE SECONDARY PRODUCTS THAN CARBIDED SURFACE

% selectivity

70
60
50
40
30
20
10
0

Fe3O4
Fe5C2

C2 olefin/C2 total   C4 olefin/C4 total   C5 plus   CH4
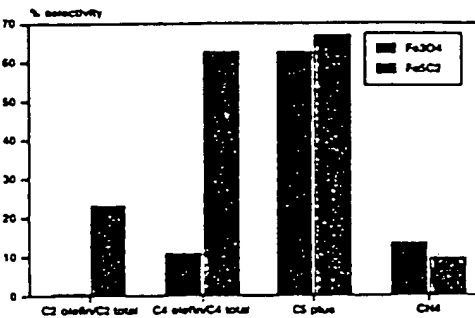
Conditions: 270°C, 75 psi, 2/1 H2/CO
1500 wt/hr, conv > 50%, CSTR

Figure 3. ALKALI PROMOTION INHIBITS SECONDARY HYDROGENATION

% selectivity

100
80
60
40
20
0

Fe5C2
Fe5C2/7%K

C2 olefin/C2 total   C4 olefin/C4 total   C10 olefin/C10 total   C5 plus   CH4
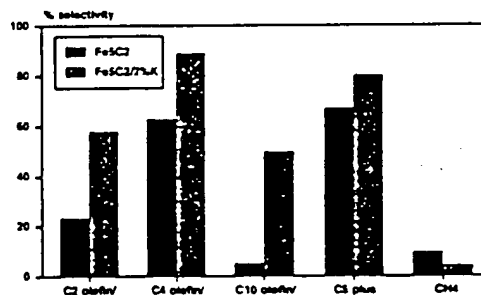
Conditions: 270°C, 75 psi, H2/CO
1500 wt/hr, conv > 50%, CSTR

Figure 4. EXCESS MATRIX CARBON DECREASES SELECTIVITY ON LASER GENERATED Fe3C

% selectivity

100
80
60
40
20
0

"High Matrix Carbon"
"Low Matrix Carbon"

C2 olefin/C2 total   C10 olefin/C10 total   C10 paraf/C10 total   C5 plus   CH4
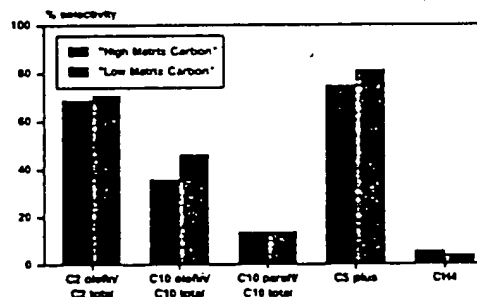
Conditions: 270°C, 75 psi, 2/1 H2/CO
1000-8000 wt/hr, CSTR
Laser Generated Catalysts

Figure 5. POTASSIUM PROMOTION HAS MINOR EFFECT ON LASER-GENERATED IRON CARBIDES

% selectivity

100
80
60
40
20
0

Fe3C
Fe3C/7%K

C4 olefin/C4 total   C10 olefin/C10 total   C5 plus   CH4

Conditions: 270°C, 75 psi, 2/1 H2/CO
8000 wt/hr, CSTR

Figure 6
COBALT SUBSTITUTION FACILITATES REDUCTION OF Fe3O4

Thermal Gravimetry: Fe3O4 Reduction

Wt. Loss

1%

Reduction Onset

Fe-Co Spinel

Fe Spinel

T (°C)

260 270 280 290 300 310

• Onset of Reduction Lowered by 20°C with Co Substitution

Figure 7
MOSSBAUER SPECTROSCOPY REVEALS DIFFERENT PHASES PRESENT IN SLURRY VS. FIXED BED REACTORS

Figure 8
CO_2 HYDROGENATION PERFORMANCE OF CARBURIZED $F_5C_2/2\%$ K

Catalyst	Comparative Fe/Cu/K/Si	Fe$_5$C$_y$/2% K With >50% wt. Matrix Carbon		
H_2/CO_2 Feed Ratio	7.0	7.0	3.0	1.7
% CO_2 Conversion	21	37	23	13
Selectivity (based on C_{1+})				
CH_4	64	16.5	6.2	4.2
C_{2+}	36	83.5	93.8	95.8
% Olefin in C_2-C_4	28	80	95	99

Conditions: 260-270°C, 3800 cm³/gFe/hr, 75 psig, 10% vol catalyst in octacosane, Parr CSTR, 30-60% vol N_2 in Feed gas

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Figure 9
CO_2 HYDROGENATION PRODUCES WIDE RANGE OF C_{10+} PRODUCTS

Catalyst: Fe$_5$C$_y$/2% K with > 50% wt. Matrix Carbon

% CO_2 Conversion	37
Selectivity (based on C_{1+})	
CH_4	16.5
C_{2+}	83.5
% Olefin in C_2-C_4	80
C_{10} Product Distribution (% wt)	
α-olefin	36.7
β-olefin	6.5
n-paraffin	13.3
n-alcohol	14.2
CH$_3$-Branched/Internal Isomers	29.4

Figure 10
LASER GENERATED IRON CARBIDES FOR SELECTIVE CO_2 HYDROGENATION

Catalyst *	FeC	Fe-Zn-C	Fe-Mn-C	Comparative Fe/Cu/K/Si
% CO_2 Conversion	22	25	31	21
Selectivity (based on C_{1+})				
CH_4	5.5	5.8	5.1	64
C_{2+}	94.5	94.2	94.9	36
% Olefin in C_2-C_4	94.0	93.0	96.0	28

Conditions: 270°C, 7/1 H_2/CO_2 3800 cm³/gFe/hr, 75 psig, 28% N_2 vol in CSTR Feed

* Laser generated Fe-Zn and Fe-Mn carbides contain <2% g atom K and <10% wt matrix carbon; laser generated Fe-C Contains No Promoters.

Figure 11
REACTION MECHANISM STUDIES VIA $^{13}CO_2$ LABELING

Reaction

$$CO/CO_2 + H_2 \rightarrow -CH_2- + -CH_2'- + H_2O$$

Observations

* Feeds with >5% (Carbon Atom) CO Feed Show No Label In Product
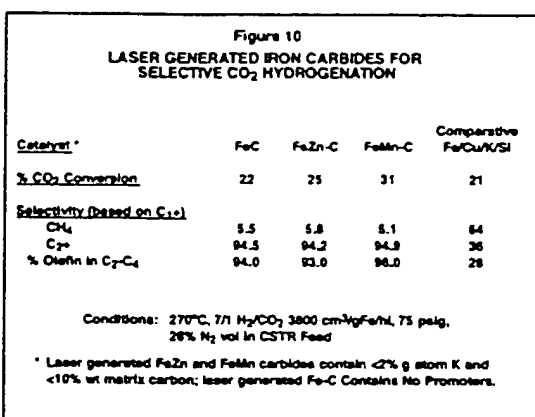* Mixed Feeds Show Labeled Product After All CO is Consumed
* CO_2/H_2 Alone Yields Mixture of Hydrocarbon Plus CO as a By-Product
* Preliminary Kinetics Suggest Two Routes for Hydrocarbon Formation
  - Reverse Shift Followed by "CO" Hydrogenation
  - Dissociative CO_2 Chemisorption Followed by "C" Hydrogenation

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Figure 12
SUMMARY

* Proprietary Iron Carbide Based Catalysts Generated for Selective Conversion of CO_2 to Liquid Hydrocarbons

  - Laser Generated Carbides that are Free of Other Metals/Metal Oxides Provide Highest Selectivity to Olefinic Liquid Hydrocarbons

* CO_2 Hydrogenation Over Iron Carbon Catalysts Provide an Efficient Means of Utilizing H_2/CO_2 Containing Streams, e.g., Process Waste Gas, Fe-Catalyzed Fischer-Tropsch Offgas

* Mechanistic Issues Remain on the Extent to Which Reverse Shift Followed by "CO" Hydrogenation Versus Dissociative CO_2 Adsorption Followed by "C" Hydrogenation Contribute to Overall Product Formation

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